

Application of combined U-Th-disequilibrium/U-Pb and (U-Th)/He zircon dating to tephrochronology

Martin Danišík ^{a,*}, Axel K. Schmitt ^{b,c}, Daniel F. Stockli ^d, Oscar M. Lovera ^c, István Dunkl ^e, Noreen J. Evans ^a

^a GeoHistory Facility, John de Laeter Centre, TIGeR, Applied Geology, Curtin University, Perth, WA 6845, Australia

^b Institute of Earth Sciences, Ruprecht-Karls-Universität Heidelberg, Im Neuenheimer Feld 236, Heidelberg D-69120, Germany

^c Department of Earth, Planetary and Space Sciences, University of California Los Angeles, 595 Charles Young Drive E, Los Angeles CA 90095, USA

^d Department of Geological Sciences, Jackson School of Geosciences, The University of Texas at Austin, 1 University Station C1100, Austin, TX 78712, USA

^e Department of Sedimentology and Environmental Geology, Geoscience Centre, University of Göttingen, Goldschmidtstrasse 3, Göttingen D-37077, Germany

ARTICLE INFO

Article history:

Received 29 February 2016

Received in revised form

15 July 2016

Accepted 21 July 2016

Available online 7 September 2016

Keywords:

U-Th-disequilibrium dating

(U-Th)/He dating

Zircon

Tephra

Tephrochronology

ABSTRACT

The combination of U-Th disequilibrium/U-Pb and (U-Th)/He dating of zircon (ZDD) has provided a relatively new radiometric approach suitable for dating Quaternary zircon-bearing volcanic and pyroclastic deposits. This approach permits the dating of zircon as young as ca. 2.5 ka and has huge potential for tephrochronology and other fields of Quaternary science. Its applicability range covers the critical time-window in Quaternary geochronology beyond the range of ^{14}C and below the limit of routine Ar/Ar dating (i.e. between ca. 50 ka and 1.5 Ma). The combined U-Th disequilibrium/U-Pb and (U-Th)/He dating approach can also be applied to other actinide-rich minerals such as allanite or monazite. In <1 Ma young volcanic samples, the integration of the low-temperature (U-Th)/He geochronometer with the high-temperature U-Th disequilibrium/U-Pb geochronometers is essential in order to correct for disequilibrium in the U-decay chains which, when ignored, may result in erroneous underestimation of true eruption ages.

In this review paper we summarize past developments and the current state of the ZDD method, explain the theoretical principles, and document the necessity of combining (U-Th)/He with U-Th-disequilibrium and/or U-Pb methods when dating young volcanic material. We then describe analytical procedures and highlight the advantages of the ZDD method. Finally, we present some examples that illustrate the efficacy of this method to derive reliable eruption ages for young tephra, and outline future directions in methodological development and application for this geochronological tool.

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1. Introduction

A prerequisite for using tephra as chronostratigraphic markers of geologic time is the knowledge of their numerical age (Lowe, 2011). Modern radiometric dating techniques suitable for dating Quaternary tephra include K/Ar (Ar/Ar), radiocarbon (^{14}C), fission-track, and luminescence methods. However, their application is often limited by (1) a scarcity of materials suitable for dating (e.g., organic material in close stratigraphic association with tephra); (2) limited timespans over which individual methods are applicable

(especially for ^{14}C); (3) open-system behaviour (e.g., mobility of K and Ar in glasses, or excess ^{40}Ar : Chen et al., 1996; McDougall and Harrison, 1999; Spell et al., 2001; changes in luminescence signal due to variable water content, or variation in dose rate: Murray and Funder, 2003); (4) mass-dependent kinetic isotopic fractionation (e.g., for Ar dating of obsidian: Morgan et al., 2009); (5) limitations in analytical sensitivity (e.g., low signal to noise ratio in the measurements, especially for fission-track counting of young materials); and (6) imperfections in the datable materials (e.g., contamination of organic matter, partial track fading, or presence of undetected xenocrysts and inclusions). Given these caveats, establishing an accurate numerical age of a tephra layer may in fact be very difficult and there is a clear need for innovative accurate and precise radiometric dating tools with which to complement

* Corresponding author.

E-mail address: m.danisik@curtin.edu.au (M. Danišík).

these existing techniques.

The combined application of (U–Th)/He dating of Quaternary zircon (Farley, 2002; Reiners et al., 2004) with $^{238}\text{U}/^{230}\text{Th}$ disequilibrium and/or U–Pb dating (Schmitt et al., 2006) is a relatively new approach that has huge potential for tephrostratigraphy and tephrochronology as it permits zircon as young as ca. 2.5 ka to be dated accurately and precisely (Schmitt et al., 2012; Danišik et al., 2012). In addition to zircon, (U–Th)/He and $^{238}\text{U}/^{230}\text{Th}$ disequilibrium dating of the thorium-rich accessory mineral allanite has been performed to date late Pleistocene tephra, although these studies did not combine both dating techniques, but rather applied them individually (Cox et al., 2012; Vazquez and Lidzbarski, 2012). The combined (U–Th)/He and U–Th–(Pb) dating technique – for simplicity hereafter referred to as ZDD (zircon double-dating) – can cover a critical time window which is important for Quaternary science, but difficult to access using other techniques. Because of its novelty in the field of Quaternary tephrochronology, this dating approach has not yet been widely used in tephra studies, despite its demonstrated ability to determine accurate and precise eruption ages for young tephra. In order to increase appreciation and application of the method, this review paper aims to provide a summary of past developments and the current state of the ZDD method to make it more accessible to geochronology users in the fields of tephrochronology and volcanology. We touch on the theoretical background and the necessity of combining (U–Th)/He with U–Th–disequilibrium and/or U–Pb methods when dating young volcanic and pyroclastic material, and briefly describe analytical procedures. Finally, we highlight advantages and present some examples illustrating the capability of this method to derive reliable eruption ages for young tephra.

2. Historical perspective and theoretical background

Zircon is an accessory mineral that crystallizes in evolved magmas as they cool, differentiate, and enrich zircon's defining stoichiometric component, zirconium, in the residual melt phase (Boehnke et al., 2013). Zircon incorporates significant amounts of U and Th (typically 100s of ppm, but concentrations can vary widely, even within individual rocks or crystals), making it uniquely suitable for dating a wide range of geological processes ranging from low (ambient) to high (magmatic) temperatures using a variety of parent–daughter pairs which differ strongly in accumulation rate and retentivity (Hanchar and Hoskin, 2003). The potential of zircon to date young volcanic rocks was recognized more than a century ago, and in fact the very first radiometric dating technique applied to zircon was the (U–Th)/He method (Strutt, 1910a). In his pioneering work, Strutt (1910a) reported U, Th and He abundances in zircons collected from young volcanic systems. However, being aware that He was leaking from the minerals over geologic time and given some obvious lack in analytical sensitivity, R.J. Strutt did not feel comfortable with conversion of the measured abundances into numerical (U–Th)/He ages as he (paraphrased) “did not wish these ages to be quoted without due regard to their provisional character” (Strutt, 1910a,b). In this respect it is worth noting that ages of <~100 ka (Mt Vesuvius, Italy), ~870 ka (Mayen, Eifel volcanic field, Germany), and ~1.5 Ma Campbell Island (New Zealand) calculated from Strutt's data are not far from the results obtained by modern geochronological methods. Another early study that used the zircon (U–Th)/He method to constrain the age of a volcanic eruption was presented by Holmes and Paneth (1936), who reported Oligocene–Miocene ages for xenocrystic zircons in kimberlites from South Africa. Following these early attempts, the interest in the (U–Th)/He method declined, and later the dating of volcanic rocks was primarily achieved using other radiometric methods such as K/Ar (Ar/Ar), fission track and radiocarbon.

The revival of (U–Th)/He methods commenced in the late 1980s with the pivotal paper on apatite (U–Th)/He dating being that by Zeitler et al. (1987). Subsequent work by groups in Heidelberg (Lippolt and Weigel, 1988; Wernicke and Lippolt, 1992, 1994a; Lippolt et al., 1993, 1994,b), at Caltech (Wolf et al., 1996, 1998; Farley et al., 1996; Farley, 2000; Reiners and Farley, 1999; Warnock et al., 1997; House et al., 1998, 1999, 2000; Stockli et al., 2000) and Yale (Reiners et al., 2002, 2004; Reiners, 2005) created the robust methodological and interpretational basis for the modern (U–Th)/He dating method.

In the modern era of (U–Th)/He geochronology, the majority of applications focused on studying rock exhumation, mountain building and landscape evolution. However, it was soon recognized that zircon is potentially useful for dating young volcanic rocks (Farley et al., 2002) and that the (U–Th)/He system can be extremely valuable for tephrochronology as it allows dating of tephra that erupted within the critical time-window between ca. 50 ka and 1.5 Ma (Farley, 2002). As noted by Farley et al. (2002), besides the analytical challenges related to the low abundances of radiogenic He in young materials, the major obstacle for high-precision (U–Th)/He dating of young tephra (and other pyroclastic and volcanic rocks) is the potential effect of secular disequilibrium in the U–decay chains, the state of which needs to be quantified or the resulting (U–Th)/He ages may be erroneously young. Subsequently, Schmitt et al. (2006) introduced a novel approach for dating young tephra, which used a combination of (U–Th)/He and U–Th–disequilibrium (or U–Pb) methods applied to individual zircon crystals, and which could address the problem of secular disequilibrium more accurately. This method has yielded accurate and precise eruption ages on volcanic rocks across the critical age range including late Holocene ages (Schmitt et al., 2012). Although this approach has received an increased attention in the past few years (Schmitt et al., 2010a,b, 2011, 2012, 2013, 2014a,b; Danišik et al., 2012; Lindsay et al., 2013; Howe et al., 2015; Gebauer et al., 2014), its full potential for tephrochronology and Quaternary geochronology in general is yet to be exploited.

3. Principles of zircon dating by the combined U–Th–disequilibrium/U–Pb and (U–Th)/He (ZDD) method

The principles of the individual radiometric techniques involved in ZDD have been described in several comprehensive review papers. Readers interested in zircon (U–Th)/He dating are referred to Farley (2002) and Reiners (2005) and, for zircon U–Th–disequilibrium and U–Pb dating, to Schmitt (2011) and Schaltegger et al. (2015). Here we briefly review these methods with an emphasis on how they can be integrated to date young volcanic and pyroclastic deposits and on the special considerations required to achieve accurate results.

The zircon (U–Th)/He geochronometer is based on the accumulation of ^4He produced by the alpha decay of ^{238}U , ^{235}U , ^{232}Th and ^{147}Sm isotopes, naturally occurring in zircon (e.g., Farley, 2002; Reiners et al., 2004). Radiogenic ^4He is extremely mobile at high temperatures and its retention in the crystal lattice of zircon occurs only at temperatures of 150–220 °C, depending on crystal size and cooling rate (Reiners et al., 2004; Guenther et al., 2013). (We note that this commonly reported temperature range is valid for spherical diffusion domains with the radius of 60 μm and cooling rates of ca. 10 °C/Ma; for quickly cooled volcanic rocks the temperature range can increase to 210–290 °C.) When applied to volcanic rocks, zircon (U–Th)/He ages thus record the time of cooling during ascent to the surface and, therefore, are interpreted as eruption ages, provided the dated material did not experience any post-eruptive reheating to the critical temperatures. Another factor that may influence the sensitivity of the zircon (U–Th)/He system is

radiation damage (Hurley, 1952; Shuster et al., 2006; Flowers et al., 2007; Guenther et al., 2013). However, this phenomenon can be reasonably ignored for young zircons (Cherniak and Watson, 2001) because it requires either extremely high U and Th abundances or long-term (>100 Ma) residence in the zircon He partial retention zone (Reiners et al., 2004; Reiners, 2005; Guenther et al., 2013).

Conventionally, (U-Th)/He ages are calculated from abundances of U, Th, He and $\pm$ Sm (alpha decay of Sm is often reasonably neglected due to its low content in zircon and minimal contribution to the total He budget) measured on single crystals by applying the “(U-Th)/He age equation” (also known as the ^4He production equation; e.g., Farley, 2002).

The calculated ages (often termed ‘raw (U-Th)/He ages’) need to be corrected to account for He loss because of alpha recoil (Farley et al., 1996). This correction (alpha ejection correction or F_t correction) primarily depends on the size, shape and density of the dated crystal, as well as on the distribution of parent nuclides. For normal sized zircons (approximately 60 μm in diameter), the F_t -corrected (U-Th)/He ages are commonly up to 30% higher than the raw (U-Th)/He ages. The F_t correction is believed by some authors to represent the major source of error affecting the accuracy of (U-Th)/He method (Farley et al., 1996; Hourigan et al., 2005; Danišik et al., 2010; Bargnesi et al., 2016) and, therefore, is particularly critical for high precision (U-Th)/He dating. Conventionally, the simplest approximation of F_t correction factors is calculated from surface areas and volumes of analysed crystals obtained from measuring their physical dimensions on a series of 2D micrographs, whereby the intra-crystal distribution of U and Th is generally assumed to be homogenous (Farley et al., 1996). Zircons, however, commonly show strong zoning in U and Th abundances (e.g., Dobson et al., 2008), which can cause deviation in conventionally calculated F_t correction factors and, where zoning is extreme, could result in age inaccuracies of up to ~35% (Hourigan et al., 2005; Reiners, 2005). Therefore, for high-precision applications of the (U-Th)/He method, it is recommended that efforts are made to characterize the U-Th distribution and to calculate the F_t correction more accurately. Viable analytical approaches that can be applied include depth profiling by laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) (Hourigan et al., 2005; Bargnesi et al., 2016), mechanical abrasion (Bargnesi et al., 2016), X-ray microtomography (Herman et al., 2007; Evans et al., 2008), and cathodoluminescence (CL) imaging or elemental mapping by LA-ICPMS (Danišik et al., 2016). A potential limitation of some of these approaches is that they require embedding and polishing of the crystals, which can make He analysis even more challenging.

The second correction that needs to be considered when dating young volcanic or pyroclastic rocks or deposits concerns the possible effect of secular disequilibrium in ^{238}U - and ^{235}U -decay chains. The ^{232}Th -decay chain includes only short-lived intermediate daughter isotopes (half-lives <7 yrs; Holden, 1990) and can be neglected. The conventional (U-Th)/He age equation assumes secular equilibrium among all daughter products in U and Th decay chains, and this assumption is valid for minerals crystallized >375 kyrs prior to the onset of He accumulation (Farley et al., 2002). For certain applications, such as dating zircon with young (<1 Ma) crystallization ages, however, the effect of secular disequilibrium on the production of ^4He must be assessed, or the ages calculated from this equation will underestimate the true eruption ages by up to a few tens of percent (Farley et al., 2002). The reason for this discrepancy lies in the slower production of He for ~375 kyrs after crystallization, prior to the establishment of secular equilibrium (after ca. five half-lives of ^{230}Th). The slower He production is related primarily to the initial deficit of the ^{230}Th (half-life of ~75.58 ka; Cheng et al., 2013) that is commonly observed in zircon due to its preferential incorporation of ^{238}U relative to ^{230}Th during

crystallization (Blundy and Wood, 2003; Farley et al., 2002). To a lesser degree, slower He production is related to the fractionation of ^{226}Ra (half-life 1.599 ka; Holden, 1990), which is relevant for samples with eruption ages of <10 ka (Farley et al., 2002). Excess of ^{231}Pa (half-life ca. 32.76 ka; Robert et al., 1969) from the ^{235}U decay chain, in contrast, is expected from the higher zircon-melt partitioning (D) values for Pa relative to U (Schmitt, 2007). As a result, excess ^{231}Pa produces He that is unsupported if radioactive equilibrium at the time of crystallization is assumed (Farley et al., 2002). Given these deviations, the amount of disequilibrium prior to eruption must be established in order to calculate an accurate eruption age. The magnitude of secular disequilibrium correction depends on the initial $^{230}\text{Th}/^{238}\text{U}$ activity ratio and magma residence time of the crystal (i.e., the time between the crystallization and the onset of He accumulation, which is the time of eruption; Farley et al., 2002). With increasing magma residence time, the effect of secular disequilibrium on the (U-Th)/He age decreases, as the U-decay system at magmatic temperatures progressively returns to equilibrium before the start of the (U-Th)/He clock after eruptive quenching (Fig. 1) (Farley et al., 2002; Reiners et al., 2004).

As demonstrated by Farley et al. (2002), the disequilibrium correction can be quantified by (U-Th)/He dating of co-genetic minerals with different Th/U ratios (e.g., zircon, apatite, monazite), which will delineate an isochron, defining the eruption age. Applying this approach to co-genetic zircon and apatite, the authors dated the Rangitawa Tephra (New Zealand) to 330 ± 10 ka (2σ), consistent with ages obtained previously by Kohn et al. (1992), Pillans et al. (1996) and Lowe et al. (2001). Although potentially useful, the application of this approach is limited due to the requirement of at least two co-genetic minerals suitable for dating and due to the variation of magma residence times among the crystals, which may introduce scatter complicating construction of a single isochron (Farley et al., 2002).

Schmitt et al. (2006) proposed an alternative approach to account for the secular disequilibrium that can overcome both problems. The method requires only one actinide-rich accessory mineral – preferably zircon – but it can also be applied to other phases such as allanite or monazite (Boyce et al., 2009; Cox et al., 2012). Single zircon crystals are “double-dated” first by the U-Th-disequilibrium method (for crystals with secular disequilibrium, i.e., crystallized at <~375 ka; Fukuoka, 1974; Fukuoka and Kigoshi, 1974; Reid et al., 1997; Lowenstern et al., 2000) or, alternatively,

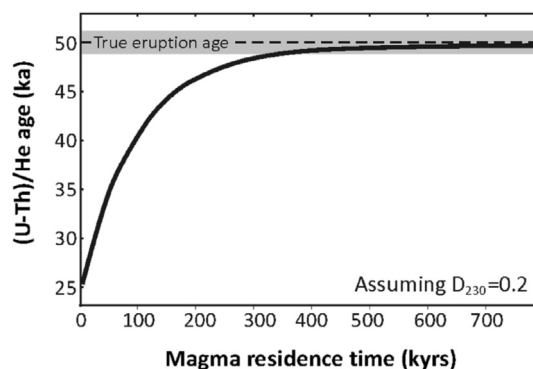


Fig. 1. The effect of magma residence time (x-axis) on measured (U-Th)/He age. The curve is calculated for a zircon crystal with true eruption age of 50 ka by assuming $D_{230} = 0.2$ which is a typical value for zircon (Charlier and Zellmer, 2000; Farley et al., 2002). The grey band is a typical analytical uncertainty for the (U-Th)/He method. Note that ignorance of a disequilibrium effect may result in underestimation of the age by up to 50% for crystals with short magma residence times. Also note that after >300 kyrs of magma residence, the effect of disequilibrium on (U-Th)/He may not be detectable.

the U-Pb method (for crystals in secular equilibrium, i.e. crystallized at >375 ka; Ireland and Williams, 2003), and then by (U-Th)/He methods. For clarity, we note that the U-Th-disequilibrium method has been variably abbreviated in the literature such as U-series, U/Th disequilibrium, $^{238}\text{U}/^{230}\text{Th}$ disequilibrium, or the U-Th method.

The application of both methods to the same crystal is feasible because of the minimal material consumption by the instrumentation used for U-Th-disequilibrium or U-Pb dating (i.e., spot analysis by ion microprobe, creating ~30- μm wide and ~5- μm deep craters), preserving enough material for subsequent (U-Th)/He dating. Unlike the (U-Th)/He system, the U-Th-disequilibrium and U-Pb systems are closed at temperatures at which zircon saturates in magmas (Cherniak et al., 1997; Cherniak and Watson, 2001) and thus record the crystallization age of zircon crystals. The combination of these methods directly constrains the magma residence time for individual zircon crystals, allowing quantification of the disequilibrium correction for (U-Th)/He age calculation (e.g., Schmitt et al., 2006, 2010b; see also Section 4.4).

3.1. Advantages of the ZDD method

The combined ZDD dating approach has a great potential for tephrochronology for several reasons as listed below.

(1) Except for the Ar/Ar method, ZDD is the only dating method that has the demonstrated ability to directly date volcanic eruptions in the range ~2500 years to >1 Ma with a fairly high precision (within a few percent). This age range encompasses the critical “blindspot” in Quaternary geochronology beyond the range of ^{14}C and below the limit of routine Ar/Ar dating (Danišik et al., 2012; Harangi et al., 2015).

(2) Zircon is essentially ubiquitous not only in the silicic volcanic rocks that dominate intra-oceanic subduction systems, but also is associated with intraplate magmatism and volcanic rifted margins (Leat and Larter, 2003). These rocks are often difficult to date by Ar-based methods due to the lack of K-rich minerals and the ZDD method may thus offer the only means for their dating. In addition, zircon crystals can often be found in intermediate, and occasionally as xenocrysts, in mafic rocks (Blondes et al., 2007; Hurai et al., 2013), and so these are potential targets for ZDD as well.

(3) Zircon is extremely resistant to physical and chemical weathering which makes dated zircons a potential correlation tool for altered (weathered) tephras that cannot be “fingerprinted” by other methods (Schmitt and Hulen, 2008).

(4) When compared with Ar/Ar dating, the (U-Th)/He system (as a part of ZDD) is intrinsically more sensitive because of the rapid accumulation of ^4He (~20-times faster than ^{40}Ar per parent nucleus), and lower backgrounds (atmospheric ^4He being 2000 times lower than ^{40}Ar ; Farley, 2002). In addition, inheritance of “excess” He from a previous history, for instance due to incomplete degassing (Spell et al., 2001), is unlikely given the high diffusivity of He.

(5) Only a small amount of material is required to obtain robust data (~5–20 single zircon crystals per sample) and so in favourable cases, volumetrically-small samples can be dated.

(6) The “default” determination of crystallization (U-Th or U-Pb) and eruption ((U-Th)/He) ages for each single zircon crystal provides a first-order internal consistency check of the method (i.e., crystallization age > (U-Th)/He age). Furthermore, the youngest meaningful age component determined from a crystallization age spectra (i.e., not the youngest analytical/geological outlier) provides a maximum limit for the eruption age. In other words, U-Th and U-Pb crystallization ages pre-date the eruption, but never directly date it.

(7) Finally, elucidating crystallization-to-eruption histories for

single crystals has applications beyond the scope of tephrochronology as these provide information on magma accumulation, storage and cooling which are essential for studying the dynamics of magmatic systems (Schmitt, 2011). Geochronological data can be further combined with isotopic and trace-element analysis that together provide a powerful tool to study compositional and thermal evolution of magmatic systems (Ferry and Watson, 2007).

4. Analytical procedures

The procedures described here are those employed for zircon (U-Th)/He dating at the University of Waikato and Curtin University and for zircon U-Th-disequilibrium/U-Pb dating at the University of California Los Angeles (UCLA) SIMS laboratory. (U-Th)/He dating in laboratories at California Institute of Technology, and universities of Kansas, Texas at Austin, and Göttingen differs in instrumentation and procedure, but not in the fundamental analytical workflow which is schematically illustrated in Fig. 2.

4.1. Sample collection and zircon separation

Sample collection for the purpose of ZDD dating follows the principles applied when sampling for (U-Th)/He thermochronology. It is recommended to collect samples of *in-situ* (non-redeposited), fresh material without signs of weathering or secondary alteration, and to avoid contamination of samples by material from surrounding rocks. To exclude the possibility of post-eruptional reheating of zircon (and potential loss of He; Mitchell and Reiners, 2003) by subsequent eruptions, wildfires or lightning, samples should be collected >30 cm away from the surface or contact with overlying units. The typical amount of material required to obtain the desired quantity of zircon depends on lithology but is typically in the range of 5–10 kg. Preferred rock types include pumice blocks/clasts, lavas, but obsidian blocks/clasts and volcanic ash may contain zircon and be favourable for dating. For ash, Stokes' law predicts that despite zircon's higher density compared to that of glass (4.65 vs. 2.3 g/cm³) the resulting size fractionation due to crystal settling is within a factor of 1.4. This means that tephra deposits with glass particles >70 μm in diameter should contain zircon suitable for ZDD (>50 μm diameter).

Zircon crystals are extracted from the samples using conventional separation procedures including rock fragmentation (e.g., by mechanical crushing or electrodynamic disaggregation), sieving and collection of the <250 μm -size fraction, washing, magnetic and gravitational separation, hand-picking of zircon crystals under a binocular microscope, and, finally, leaching of the crystals in concentrated HF for ~3–5 min to remove adherent glass. From the pure zircon concentrate, the most suitable crystals for ZDD dating are selected using optical microscopy based on their morphology, size and absence of crystal imperfections (Farley, 2002; Reiners, 2005). Preferably only euhedral, intact, clean, inclusion- and defect-free crystals in the form of tetragonal or octagonal prisms with bipyramidal or pinacoidal terminations and widths of >50 μm are selected in order to facilitate calculation of the most accurate alpha ejection correction (Farley, 2002). Although reasonably precise ages have been obtained by ZDD from as few as five zircon crystals (see, e.g., Schmitt et al., 2011), we recommend selecting at least 20 crystals in order to allow for characterization of U-Th distribution (see below), compensate for potential losses during the remaining analytical steps and to achieve statistically more robust results.

Although thorough zircon characterization is currently not a part of the routine analytical procedure in (U-Th)/He dating, for reasons described in Section 3, we do recommend characterizing

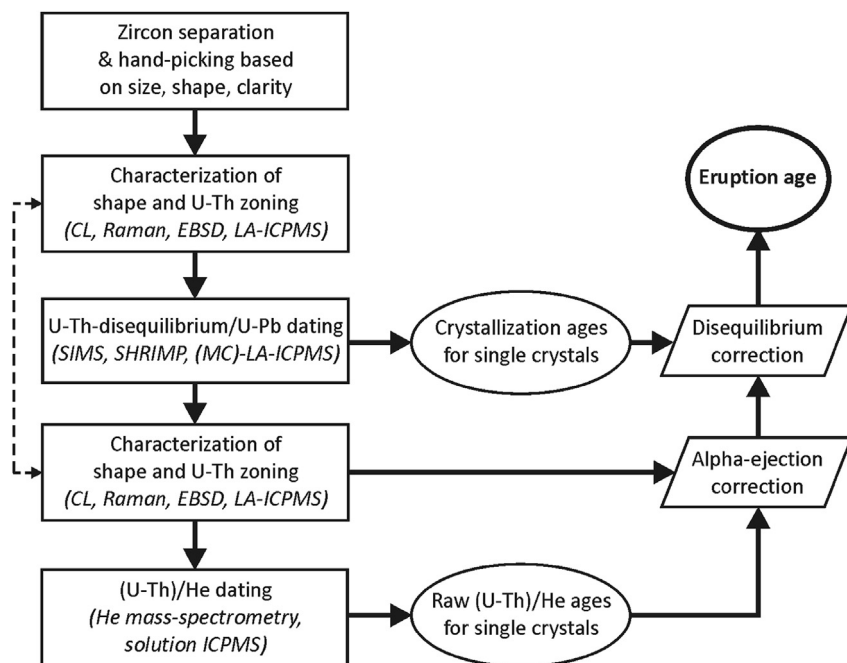


Fig. 2. Flow chart showing steps recommended for combined U-Th-disequilibrium/U-Pb and (U-Th)/He dating. Note that characterization of zircon crystals for U-Th distribution and physical dimensions required for F_t correction can be undertaken before or after the U-Th-disequilibrium/U-Pb dating step.

the interiors of selected crystals for U-Th zoning either prior to or after the determination of crystallization ages (see next section). A range of non-to semi-destructive techniques including CL, electron backscatter diffraction, Raman spectroscopy, mapping or profiling by LA-ICPMS or ion microprobe can serve this purpose.

4.2. U-Th-disequilibrium and U-Pb dating

Determining the crystallization age (and constraining the magma residence time) is one of the key parameters in the disequilibrium correction calculation and this age needs to be measured for each individual zircon crystal. This is because zircon crystallization occurs over extended periods of time and pre-eruptive crystal residence time can vary within a population of zircon crystals (e.g., Reid et al., 1997; Charlier and Zellmer, 2000). Viable analytical instrumentation that facilitates minimum consumption of analysed material, allowing subsequent dating of the same crystal by (U-Th)/He methods, includes high-resolution ion microprobes (secondary ionization mass spectrometers – SIMS – or sensitive high resolution ion microprobes – SHRIMP; Schmitt et al., 2003, 2011; Charlier et al., 2005) which sputter material from 30- μm wide and 5- μm deep craters. It is also possible to use multi-collector laser ablation inductively coupled plasma mass spectrometry (MC-LA-ICPMS) which utilizes pits 50 μm wide and 10 μm deep (Stirling et al., 2000; Bernal et al., 2014; Guillong et al., 2016). Although this latter approach has not yet been tested in ZDD, it may offer a more cost- and time-effective option over ion microprobes. Bulk dissolution techniques such as isotope dilution thermal ionization mass spectrometry (ID-TIMS) are not suitable for U-Th-disequilibrium and U-Pb geochronology because it precludes subsequent analysis of He.

In previous studies, crystallization ages for zircon crystals were determined on a CAMECA ims1270 ion microprobe at UCLA following the procedures outlined in Schmitt (2011). In brief, entire zircon crystals are pressed into indium metal with their prism faces levelled with the surface together with pre-polished fragments of the AS3 secular equilibrium reference zircon (Duluth Gabbro,

1099 Ma; Paces and Miller, 1993). Indium is used because of its exceptional softness permitting easy recovery of the crystals, and also because it helps to orientate the crystals' prism faces parallel to the surface during pressing. The surface of the sample mount is coated with a conductive layer of gold and analysed under bombardment with an energetic (23 keV impact energy, tens of nA current) $^{16}\text{O}^-$ ion beam. Positive secondary ions are detected either in single-collection or dynamic multi-collection mode using combinations of Faraday cups (for major oxide species $^{232}\text{ThO}^+$ and $^{238}\text{UO}^+$) and electron multipliers (for $^{230}\text{ThO}^+$ and backgrounds, Pb^+ isotopes, and other ion species with intensities $<10^6$ cps). $^{238}\text{U}/^{230}\text{Th}$ and U-Pb analysis is typically performed on the outermost growth layers of zircon to determine the final stage of crystallization, possibly the end-point of a long evolution from secular equilibrium to disequilibrium in U-decay chains. Crystallization ages for zircons in U-series disequilibrium are calculated as two-point model isochrons through the measured isotopic composition of zircons and a model melt composition that can be approximated by bulk analysis of U and Th abundances in whole rocks or glass (Reid et al., 1997; Vazquez and Reid, 2004). The accuracy of the U-Th method has been established by interlaboratory comparison of a ca. 12 ka zircon reference from Puy de Dome (France) determined by isotope dilution mass spectrometry and alpha spectrometry (Condomines, 1997) in several labs and by different methods (Schmitt et al., 2010c; Wright et al., 2015; Guillong et al., 2016). Crystallization ages for zircons in secular equilibrium (>380 ka) are calculated from measured U/Pb isotopic ratios following corrections for common Pb and initial disequilibrium (e.g., Schmitt et al., 2003). Accuracy is confirmed by analysis of reference zircons (e.g. Schaltegger et al., 2015).

Following SIMS analysis, zircon crystals are removed from the indium mounts for (U-Th)/He dating. When sufficient crystals in a sample have been analysed by SIMS, it is advised to preferentially select crystals in secular equilibrium or, if in disequilibrium, crystals with older crystallization ages for (U-Th)/He dating. This preferential selection is desirable because crystals with older crystallization age will have a smaller disequilibrium correction and a lower

resultant age uncertainty (Schmitt et al., 2014a).

4.3. (U-Th)/He dating

The (U-Th)/He portion of ZDD dating traditionally follows the conventional ‘whole-grain’ (U-Th)/He dating approach in which the entire single zircon crystal is analysed for bulk U, Th, $\pm$ Sm and He content (Evans et al., 2005; Danišik et al., 2012). We note, however, that a new *in-situ* approach based on laser spot analysis (Boyce et al., 2006, 2009; Vermeesch et al., 2012; Tripathy-Lang et al., 2013; Evans et al., 2015) may offer another viable option for ZDD dating in the future (see also Boyce et al., 2009).

In conventional (U-Th)/He dating, zircon crystals previously analysed by SIMS are photographed under a microscope and measured (in 3D) in order to calculate the alpha ejection correction (Farley et al., 1996). Crystals are then loaded in Nb microtubes, degassed at ~ 1250 °C under ultra-high vacuum using a focused ~ 980 -nm diode laser beam and analysed for ^4He on a noble-gas mass spectrometer (Pfeiffer Prisma™) by isotope dilution using a ^3He spike. A major analytical challenge in He analysis is the low abundance of radiogenic ^4He in young zircon, which is often close to the analytical detection limits of standard He extraction systems. At Waikato University, special care was taken to keep the He extraction line as clean as possible by avoiding analyses of old, hydrous mineral phases, minimizing any possibility of contamination and regular baking-out of the tubing. He abundances measured in young zircons were commonly 0.01 nano cubic centimetres (ncc), and in extreme cases, 0.001 ncc levels at STP (Schmitt et al., 2012, 2014a). Achieving the desired precision ($<3\%$ relative error) on such low ^4He volumes involved complete degassing of analysed crystals, thorough cleaning of the released gas, low and reproducible analytical blanks measured before and after an ‘unknown’, and monitoring and correction for isobaric interferences on the masses of interest.

Following He measurements, zircon-Nb packages are retrieved from the He extraction system, spiked with ^{235}U and ^{230}Th , and dissolved in pressure digestion vessels (Parr bombs) using HF-HNO₃ and HCl acids (Evans et al., 2005). Complete dissolution of young volcanic or pyroclastic zircons may require a longer time than usual bomb treatment during the HF-HNO₃ bombing stage (at least 60 h). Dried down and diluted solutions are then analysed by isotope dilution for U, Th and by external calibration for Sm on ICPMS (Agilent 7500). U, Th and Sm abundances are calculated from time-resolved data corrected for drift, background, blanks and outliers.

From the measured abundances of U, Th, Sm and He, a ‘raw’ (U-Th)/He age is calculated for each zircon crystal based on the (U-Th)/He age equation (Farley, 2002). Uncertainty of raw (U-Th)/He ages is calculated from the analytical uncertainties on U, Th, He and Sm measurements and typically is in the range of 2–5% (1 sigma). The accuracy of the analytical procedure is monitored by analysing zircon age standards (e.g., Fish Canyon Tuff, reference zircon (U-Th)/He age $\pm 2\sigma$ uncertainties: 28.3 ± 2.6 Ma, Reiners, 2005, or 28.3 ± 0.8 Ma, Gleadow et al., 2015). Raw (U-Th)/He ages are then corrected for He loss due to alpha recoil following the methods of Farley et al. (1996) or Hourigan et al. (2005), depending on the availability of information on intra-grain U-Th distribution (Fig. 3). The uncertainty associated with the F_t correction factor calculation is propagated into the total uncertainty of the F_t -corrected (U-Th)/He ages.

4.4. Disequilibrium correction and eruption age calculation

As explained in Section 3, F_t -corrected (U-Th)/He ages calculated from the conventional (U-Th)/He age equation (Farley, 2002) that

assumes U-series secular equilibrium will significantly underestimate true (U-Th)/He ages, and therefore must be corrected for the effect of disequilibrium. The disequilibrium correction will depend on the magma residence time and also on the zircon-melt fractionation of ^{230}Th and ^{231}Pa relative to U (Farley et al., 2002; Schmitt et al., 2012).

The secular disequilibrium correction on final (F_t -corrected) (U-Th)/He ages (Fig. 3) can be calculated using a user-friendly Monte Carlo simulation (MCHCalc, written by O. M. Lovera and freely available at <http://sims.ess.ucla.edu/Research/MCHCalc.php>; Schmitt et al., 2010b). The required input parameters include F_t -corrected (U-Th)/He ages and uncertainties, zircon crystallization ages and uncertainties, and so-called D_{230} and D_{231} parameters describing zircon-melt fractionation of $^{230}\text{Th}/^{238}\text{U}$ and $^{231}\text{Pa}/^{235}\text{U}$ (Farley et al., 2002; Schmitt et al., 2010b). D_{230} can be calculated from measured data as $(\text{Th}/\text{U})_{\text{zircon}}/(\text{Th}/\text{U})_{\text{melt}}$ where $(\text{Th}/\text{U})_{\text{melt}}$ is the whole-rock or glass composition. D_{231} is commonly assumed to be ~ 3 , based on the published Pa/U zircon-rhyolite melt partitioning ratio (Schmitt, 2007). Based on these inputs, and pairing crystallization ages with (U-Th)/He ages from the given probability distributions for each datum, MCHCalc calculates probability density functions for individual disequilibrium corrected (U-Th)/He ages and propagated uncertainties. By doing so the algorithm rejects any pairing which violates the constraint that the eruption age must post-date crystallization age, and repeats the calculation until a pre-defined number of iterations has been reached. Finally, since a volcanic eruption represents an instantaneous geological event, from the resulting distribution of all individual (U-Th)/He ages, MCHCalc allows to calculate the most likely eruption age (termed as ‘concordant’ eruption age or ‘best-fit’ eruption age in Schmitt et al., 2010b, and Danišik et al., 2012, respectively) and associated uncertainty for the entire population (Fig. 3). Importantly, the software also estimates a goodness-of-fit parameter – Q (or GoF), using the incomplete gamma function (Press et al., 2002). Q values $> 10^{-4}$ are accepted as valid for averaging. Because the (U-Th)/He ages corrected for disequilibrium represent a multi-component dataset that may display complexities such as anomalous ‘outliers’ that may potentially skew the final result, it is strongly recommended to critically analyse and evaluate the data and not use MCHCalc simply as a black-box.

5. Case studies: ZDD application to tephrochronology and comparison with other methods

The ZDD method was introduced ten years ago and, although its major focus of application has been in studying the dynamics of young magmatic systems (Schmitt et al., 2006, 2010a, b, 2011; 2013, 2014a, b; Lindsay et al., 2013; Gebauer et al., 2014; Howe et al., 2015), the potential of the ZDD method for tephrochronology is undisputable. The following are summaries of several studies that illustrate the application of ZDD in tephrochronology and demonstrate its capability to produce accurate ages that agree with ages obtained from other dating techniques.

In their pioneering work, Schmitt et al. (2006) dated the eruption of La Virgen tephra from the Las Tres Virgenes volcano (Baja California) by ZDD at 36 ± 6 ka (2σ), and later refined this age to 30.7 ± 1.6 ka (2σ) by employing an improved analytical protocol and data reduction scheme, including use of the MCHCalc software (Schmitt et al., 2010b). This new result for the eruption of La Virgen tephra was significantly older than previously postulated historic (based on a Mission-period map) or Holocene (based on a single ^{14}C charcoal age; Capra et al., 1998; cf. Schmitt et al., 2006, 2010b) eruption ages. The validity of the new ZDD-based eruption age was supported by ^3He and Ne exposure ages of ca. 26 ka obtained from an overlying basaltic lava flow (Schmitt et al., 2012).

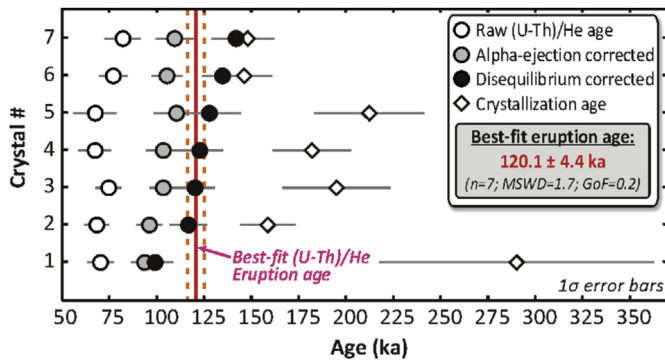


Fig. 3. An example of eruption age calculation from (U-Th)/He and U-Th-disequilibrium ages and the effect of F_t and disequilibrium corrections on final eruption age calculated using MCHCalc (Schmitt et al., 2010b). Data adopted from Schmitt et al. (2011) (sample ALA-4); uncertainties of 1σ are shown for clarity. Note the effect of magma residence time on magnitude of the disequilibrium correction for individual crystals.

Another application of ZDD in a similar age range was dating the eruption of Belfond Tuff (Saint Lucia, Lesser Antilles). In this case, ZDD ages of 21.0 ± 2.3 ka and 20.7 ± 1.4 ka (both uncertainties at 2σ) in Schmitt et al. (2010a) are indistinguishable from published ^{14}C charcoal ages of ca. 20 cal ka (Lindsay, 2002).

The first Southern Hemisphere application was by Danišik et al. (2012) who used ZDD to resolve the longstanding debate about the age of Rotoehu Ash, which is an important regional chronostratigraphic marker horizon on the North Island of New Zealand and in the south-west Pacific Ocean (e.g. Berryman, 1992; Molloy et al., 2008; Nilsson et al., 2011; Shane et al., 2006). The Rotoehu Ash is a defined (fallout) member of the Rotoiti Tephra Formation that also includes the co-eval Rotoiti Ignimbrite member (Froggatt and Lowe, 1990). We refer to both of these hereafter as 'Rotoiti tephra'. Prior to the study of Danišik et al. (2012), dating of the Rotoiti tephra has been attempted by 14 published studies, employing nine different geochronological approaches (cf. Danišik et al., 2012). This plethora was mainly due the proximity of Rotoiti age to the conventional limit of the ^{14}C method and the fact that the tephra lacks mineralogical phases suited to conventional dating methods. The ZDD based eruption age of 45.2 ± 3.3 ka (2σ) is ca. 16 kyrs younger than the previously accepted age determined by Ar/Ar dating obsidian from a distal overlying unit (Wilson et al., 2007). This new ZDD age first met with scepticism, despite being in good agreement with the ZDD age of the subsequently erupted Earthquake Flat tephra (45.2 ± 2.9 ka (2σ)) dated by the same method, high-precision ^{14}C ages from bracketing horizons (44.8 ± 0.3 and 47.5 ± 2.1 ka cal BP (both 1σ)), and with some of the previously published estimates based on palynology, luminescence dating of enclosing sediment, and sedimentation rates in terrestrial and marine settings (Danišik et al., 2012). Subsequent studies of Rotoiti deposits (Rubin et al., 2016) yielded U-Th zircon ages that were consistent with the ZDD eruption age, but in violation of the older Ar/Ar age. In parallel, Ar/Ar dating of K-feldspar and biotite from granitoid clasts erupted as part of the Rotoiti Ignimbrite were interpreted to indicate an eruption at 47.4 ± 1.5 ka age (2σ) (Flude and Storey, 2016), thus lending additional credibility to the ZDD result. Flude and Storey (2016) also discussed possible explanations why the Wilson et al. (2007) Ar/Ar obsidian age was overestimated by 10–15 ka.

Another application in a similarly critical age range was dating of the "MK-202" tephra from Ciomadul volcano (Southern Carpathians, Romania), which is possibly a correlative of a tephra found in a Black Sea drill core >1000 km to the east of the source (Cullen

et al., 2014). The "MK-202" tephra was dated to 38.9 ± 1.7 ka (2σ) by ZDD (Harangi et al., 2015). This age is in excellent agreement with the ages of 43.3 ± 3.0 ka and 35.9 ± 2.9 ka (2σ) obtained by infrared stimulated luminescence dating of feldspar from underlying and overlying horizons, respectively. These ages revealed that volcanic activity in this area is > 200 kyrs younger than that inferred from K/Ar and Ar/Ar data on biotite (cf. Harangi et al., 2015), which likely reflect excess Ar (e.g., Hora et al., 2011). In the same study, Harangi et al. (2015) also reported a ZDD age of 32.6 ± 1.0 ka (2σ) for a pumiceous pyroclastic flow deposit from the southern margin of the Ciomadul volcano (sample MK-5), which agrees excellently with the ^{14}C charcoal age of 31.5 ± 0.3 ka cal BP (1σ) (Harangi et al., 2010).

As the youngest ZDD case study so far, Schmitt et al. (2012) reported a 2480 ± 470 a (2σ) eruption age for the South Red Island rhyolite dome in the Salton Trough (California). They extracted comparatively large zircon crystals from a co-genetic granophyre clast, and replicated (U-Th)/He zircon ages in two different labs. Subsequent high-spatial resolution U-Th zircon rim analyses from the host lava by another research group yielded a maximum age for the eruption of South Red Island of 2.4 ± 1.0 ka (2σ) and overlapping but less precise Ar/Ar anorthoclase ages of 0.9 ± 2.8 ka (2σ) (Wright et al., 2015), thus confirming the ZDD age, and providing the first multi-method radiometric age evidence for a Holocene eruption in the region.

6. Summary and future perspective

Combined U-Th disequilibrium/U-Pb and (U-Th)/He dating of zircon (ZDD) is a radiometric method suitable for dating Quaternary zircon-bearing volcanic and pyroclastic deposits. The integration of the high-temperature U-Th disequilibrium/U-Pb geochronometers with the low-temperature (U-Th)/He geochronometer is essential for correcting the effects of disequilibrium in the U-decay chains on He production, which, when ignored, may result in erroneously young eruption ages. Moreover, the integration provides a first-order test for the accuracy of the ages: violation of the constraint that the U-Th disequilibrium or U-Pb age (i.e., age of crystallization) must pre-date the (U-Th)/He age (i.e., age of eruption) would reveal analytical or interpretative flaws.

In addition to volcanology, igneous petrology and Quaternary geochronology, the ZDD method has great potential for tephrochronology as it permits dating of many previously undatable tephtras, or precise and accurate re-dating of tephtras of questionable age. This advance allows previously inaccessible geological archives to be targeted, in particular those occurring in the critical time interval between ca. 50 ka and 1 Ma. For volcanic environments where magma compositions are favourable for zircon saturation, such as subduction-related silicic volcanic centres, this method offers a means to develop a high-precision tephrostratigraphic framework spanning well beyond the conventional limits of the ^{14}C method. For example, numerous regionally important, yet undated, silicic tephtras from the ca. 50 ka to 1 Ma dating gap in the exceptional tephrostratigraphic record of New Zealand offer ideal targets for this method.

The efficacy of the method has been demonstrated in several studies (see Section 5) and we consider this methodology when applied to young volcanic and pyroclastic rocks to be beyond its infancy, and rather a now mature instrument in the Quaternary geochronologists' tool kit. It remains important to conduct cross-validation experiments where eruption ages obtained using ZDD can be compared with the results from other techniques (e.g., high-precision Ar/Ar or ^{14}C dating; Mark et al., 2010; Hogg et al., 2012), and to develop reference samples in the age range between ca. 50 ka and 1 Ma for ZDD interlaboratory comparison. One

methodological limitation, potentially affecting the accuracy of (U–Th)/He eruption ages, is insufficient characterization of the distribution of parent nuclides in dated crystals. Our future developments will therefore focus on the development and testing of new analytical routines (e.g., SEM imaging, Raman mapping, LA-ICPMS mapping and profiling) to allow precise characterization of U–Th distribution in dated zircons and hence provide more comprehensive corrections for alpha recoil that should lead to better accuracy. There is also potential in further developing cost- and time-effective technologies (e.g., MC-LA-ICPMS and *in-situ* (U–Th)/He dating) to increase sample throughput and strengthen the statistical basis for age interpretation. Lastly, the development of alternative X double-dating (XDD) techniques (with X as a placeholder for actinide-rich mineral phases besides zircon) will open additional applications in tephrochronology.

Acknowledgements

This work is supported by ARC Discovery funding scheme (DP160102427), the AuScope NCRIS2 program and Australian Scientific Instruments Pty Ltd. The ion microprobe facility at UCLA is partly supported by a grant from the Instrumentation and Facilities Program, Division of Earth Sciences, National Science Foundation. We thank D.J. Lowe, C. Lane and R. Grün for editorial handling, and A. Gleadow, Sz. Harangi, and D.J. Lowe for constructive comments.

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